DRUG DEVELOPMENT AND INDUSTRIAL PHARMACY, 15(4), 649-653 (1989)

pH MEASUREMENT OF FLAME-HYDROLYSED SILICA SUSPENSIONS

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ABSTRACT

Various pH measurements on silica suspensions have been made. The changes in pH of HCl/NaOH solutions caused by increasing amounts of dispersed phase were determined. The differences in pH between the suspensions and their supernatants were also measured. The reasons for these differences are discussed and the most suitable method for pH measurement outlined.

INTRODUCTION

The measurement of the pH of suspensions is not a straightforward matter. Determination of the pH of the continuum before dispersion of the solid phase (1) neglects possible adsorptive loss of ions onto the solid surface. Direct measurement of the suspension (2) can cause error due to the suspension effect, although this may be avoided by centrifugation prior to measurement. The theoretical background to these sources of error is well established in the colloid science field but receives less attention in pharmaceutical work. Most studies refer but vaguely to the method used for pH measurement.

We have undertaken a brief study of pH measurement in some model silica suspensions, namely those of hydrophilic and hydrophobic Aerosil 200. The results should be of interest to the industrial pharmacist struggling to formulate suspensions.

MATERIALS AND METHODS

The flame-hydrolysed silica Aerosil 200 (Degussa) was used as received. Three hydrophobic silicas were prepared as described before (2). Butyldimethyl silica (C3) of surface coverage 0.255, dodecyldimethyl silica (C12) of surface coverage 0.148 and octadecyldimethyl silica (C18) of surface coverage 0.131 were made. Water was double glass-distilled and NaOH and HCl were used as received (Fisher Scientific).

Solutions of pH 1-5 were prepared from HCl and of pH 6-11 from NaOH. The pH of each solution (pH_b) was measured under filtered, oxygen-free nitrogen at 25° using a combination gel-filled glass electrode (Model E-5M, Fisher) and a microprocessor meter (Model 811, Orion Research). The pH-readings fluctuated by <0.02 over 10 mins, the stabilisation times varying from 10 to 90 mins, depending on ionic strength. Suspensions were then prepared by dispersing silica in each continuum using a Model B12 Ultrasonic Cell Disruptor (Branson). The pH of each suspension was measured (pH_s), after which it was centrifuged for 30 mins at 30,000rpm before the pH of the supernatant was determined (pH_e). The change in pH of the continuum caused by addition of the silica was thus:

$$\Delta pH_{b/e} = pH_b - pH_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1),$$

and the difference in pH between a suspension and its supernatant was:

$$\Delta pH_{s/e} = pH_s - pH_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2).$$

Three concentrations of Aerosil 200 were examined (0.1%, 0.5% and 2.5%), and a single concentration of each of the hydrophobic silicas (2.5%).

RESULTS

All data are presented as graphs of $\Delta pH_{s/e}$ or $\Delta pH_{b/e}$ versus pH_e. The $\Delta pH_{s/e}$ values for 0.1% Aerosil (Fig. 1a) tend to change from negative to positive with increasing pH_e, with a minimum at at pH_e of 7. This effect is more pronounced with 0.5% and 2.5%

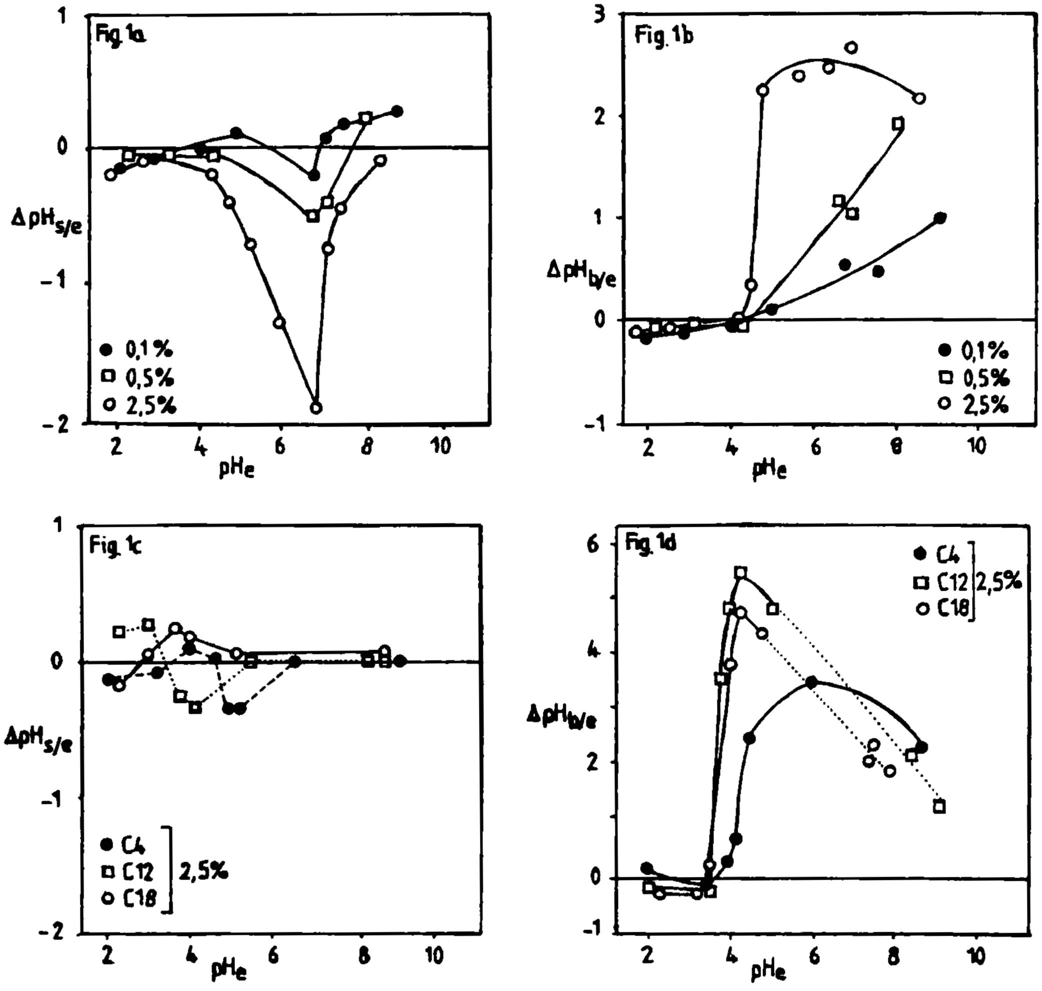

FIGURE 1

Aerosil. The $\Delta pH_{b/e}$ values become positive after pH_e of 4 (Fig. 1b), being more or less proportional to Aerosil concentration.

The $\Delta pH_{s/e}$ values for the hydrophobic silicas are scattered (Fig. 1c), but distinctly smaller than those for Aerosil 200. The $\Delta pH_{b/e}$ values are, however, substantially larger than those for Aerosil 200 (Fig. 1d), with C12 and C18 being greater than C4.

DISCUSSION

It is clear that considerable differences in measured pH occur between the original continua, the corresponding suspensions and their supernatants. One must consider which measurement most accurately reflects the hydrogen ion activity of the continuous phase.

$\Delta pH_{s/e}$ is caused by the suspension effect, whereby there is a difference in measured pH between a suspension containing charged particles and its supernatant. This is not due to differing hydrogen ion concentrations (3). The presence of charged particles in a conducting medium increases the transport number (n) of counter -ions and decrease that of co-ions. The liquid junction potential (Ej) across the salt bridge of the electrode is, however, directly related to n:

$$Ej = -\frac{RT}{F}\int_{\alpha}^{\beta} \frac{n}{z}\, d(\ln a\ ) \approx (n_{+} - n_{-})\,\frac{RT}{F}\,\ln\frac{a_{\alpha}}{a_{\beta}} \quad ......(3),$$

where z is the valency and a the activity of all ions in the region α-β between salt bridge and bulk liquid. The silica surface carries a negative charge at pHs $>$2.5, with positive counter-ions and negative co-ions in the surrounding continuum. Thus n_{+} will be greater and n_{-} smaller in a silica suspension than in its supernatant, and, as shown by Eq. 3, the Ej of the suspension will be higher. This results in a lower measured pH for the suspension, making $\Delta pH_{s/e}$ negative, as seen predominantly in Fig. 1a.

The suspension effect at small surface charges ($\S_o$) can be related qualitatively to the solid volume fraction (ϕ), particle radius (r) and the Debye-Hückle parameter (K)(4):

$$\Delta\ pH = \frac{6\phi}{1-\phi}\cdot\frac{\S_o}{Kr} \quad ....(4).$$

Hence $\Delta pH_{s/e}$ increases with increasing silica concentration or with increasing pH_e. The latter is due to the increasing surface charge on silica at pHs $>$2.5 (5). The subsequent decrease at $pH_e \gtrsim 6.5$ occurs despite continued increasing surface charge, and is presumably related to the increasing ionic strength. The small $\Delta pH_{s/e}$ values for the hydrophobic silicas may be due to their poor dispersion in water (2).

$\Delta pH_{b/e}$ is a direct measure of the change in hydrogen ion activity of the continuum occasioned by addition of the solid phase. In general a decrease in pH occured (i.e., $\Delta pH_{b/e}$ is positive), becoming larger with increasing pH_e. This is certainly due to loss of OH^- from the continuum by adsorption onto the silica surface, which occurs in increasing amounts as the pH increases (5). The high $\Delta pH_{b/e}$ values for the hydrophobic silicas are most likely due to the hydrolysis of physically-adsorbed chlorosilane molecules on the silica surface. This releases HCl, thus reducing the pH.

These results confirm that pH_e is the most reliable measure of the hydrogen ion activity of a suspension. Indeed, it is just this pH which influences surface charge and, in some cases, suspension stability. Although error due to the suspension effect will depend on the nature of the solid phase, inexact pH measurements must be expected. Error due to measurement of the continuum alone will certainly be influenced by any buffer ions present.

ACKNOWLEDGEMENTS

We thank the Campus Research Board of the University of Illinois at Chicago for financial assistance.

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